

Can Ordinary Cyclic Voltammetry provide Reliable Electrode Kinetic Data? A Comparison with Other Methods

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The difficulties in the determination of the baseline from which to measure the current on the reverse scan of a cyclic voltammogram give rise to considerable uncertainty in the peak current ratios. This source of error can be minimized by a redefinition of the peak current ratio. After subtracting the double layer charging current, the ratio R_I is defined as $R_I = |I_p^r/I_f^p|$. For Nernstian charge transfer R_I varies between 0.5726 and 0.8001 as E_λ , the difference in switching and reversible potentials, is changed in the range, 100 to 500 mV, respectively. The normalized ratio $(R_I)_N$ is defined as the observed value divided by the theoretical value for Nernstian charge transfer at the appropriate value of E_λ . The method is demonstrated with model systems and compared to other electrode kinetic methods for the determination of rate constants for reactions coupled to charge transfer. It is concluded that the method is quantitative as long as the assumption is valid that the baseline current is due only to double layer charging, and this is constant in the potential region where the peaks are located.

Cyclic voltammetry (CV) is without doubt the most widely used relaxation method for the study of electrode processes. Although the theory has been extensively developed,¹⁻¹³ the experimental data usually obtained are highly qualitative and not suitable for kinetic studies. One of the most important difficulties associated with obtaining quantitative cyclic voltammetric data involves the determination of the baseline from which to measure the current on the reverse scan. Although a number of methods to approach this problem have been presented over the years¹⁴⁻¹⁶ a satisfactory solution has not been demonstrated. On the other hand, analog differentiation of the current-potential response gives rise to a waveform suitable for quantitative analysis.¹⁷

But the fact remains that ordinary CV, with the severe baseline problem, is still the most commonly used form.¹⁸ It is the purpose of this paper to examine an alternative procedure for handling CV data. The method assumes that only faradaic and double layer charging current are present and that the double layer charging current for the return scan is equal but opposite in sign to that for the forward scan. The value of the peak current on the reverse scan, after subtracting the double layer charging current, is used to determine the peak current ratio. A similar method was proposed recently without taking into account the double layer charging current.¹⁹

EXPERIMENTAL

Reagents. The supporting electrolyte and solvent were purified by standard procedures. Fluoren-9-one and 9-cyanoanthracene were reagent grade and recrystallized before use. No electroactive impurities could be detected.

Instrumentation and Data Handling Procedures. The potentiostat was a PAR model 173D driven by a PAR model 175 function generator. A PAR 189 selective amplifier was used either as an analog differentiator or as a low pass filter. The data were digitized by a Nicolet 1090 AR digital oscilloscope interfaced to a Hewlett Packard 9825A desk computer. The computer was programmed to find the baseline for the forward scan, the peak potentials and current, and to subtract the appropriate charging currents from the peak currents for ordinary cyclic voltammetry. The derivative CV and double potential step data were handled in the normal manner.

The Electrochemical Cell. The measurements were conducted on DMF solutions containing substrate (1–1.6 mM) and Bu_4NBF_4 (0.10 M). The working electrodes were prepared by sealing small diameter platinum wire in glass and polishing to a planar surface. Reference electrodes were Ag/AgNO_3 (0.01 M) in acetonitrile separated from the main cell compartment by porous glass. Leakage from the reference electrodes was negligible as was the current flow using the small electrodes, which allowed for the use of a simple cell consisting of a cylindrical (25 ml volume) tube, fitted with a joint to accommodate a teflon electrode holder equipped with an inlet for purified nitrogen.

RESULTS AND DISCUSSION

Providing that the double layer charging current is negligible, the baseline for the return scan of a cyclic voltammogram can be approximated by a number of published procedures.^{14–16} Under these conditions, the peak current ratio, I_f/I_r , is unity for a Nernstian charge transfer reaction in the absence of complications such as coupled chemical reactions. However, during the study of electrode kinetics by CV these ideal conditions are seldom encountered. The double layer charging current is not generally negligible and the processes under study often include coupled homogeneous chemical reactions. A typical cyclic voltammogram for such a process is illustrated in Fig. 1. The process is the reduction of 9-cyanoanthracene (1.6 mM) in *N,N*-dimethylformamide (DMF) containing Bu_4NBF_4

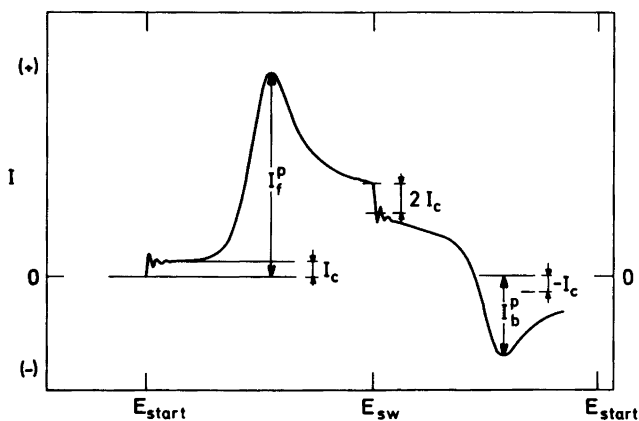


Fig. 1. Cyclic voltammogram for the reduction of 9-cyanoanthracene in DMF containing Bu_4NBF_4 (0.1 M) and HOAc (8.8 mM) at a mercury electrode. The sweep rate was 100 V/s and the amplitude of the triangular wave was 0.600 V. The peak currents (I_f and I_r) and the capacitive current (I_c) are measured from O. At E_{sw} , I_c changes sign.

(0.10 M) at a sweep rate (ν) of 100 V/s. In this case the double layer charging current is appreciable and the peak height on the return scan is diminished due to a dimerization of the anion radical. It is possible to estimate a baseline for the return scan but not without introducing considerable error in the peak current ratio. This is one reason that CV is generally considered to be a qualitative method.

There is a simple alternative which greatly reduces the error in the peak current ratio. If the requirement that the peak current ratio for the no-reaction case be equal to unity is removed, I_p^R can be measured from zero current.

For clean electrode processes, *i.e.* those on which quantitative electrode kinetic studies can be carried out, the baseline current consists only of the capacitive current (I_c) necessary to charge the electrical double layer. Thus, the peak current ratio is given by eqn. (1) when I_c is constant over the potential region between E_p^F and E_p^R . When this is not the case eqn. (1) must be adjusted

$$R_I = |(I_p^R + I_c) / (I_p^F - I_c)| \quad (1)$$

accordingly. In eqn. (1) I_p^F and I_c are taken to be positive and I_p^R is negative so that the ratio is negative as well and it is more convenient to take the absolute value for R_I .

Obviously, R_I defined by (1) will not be equal to unity under any circumstances. The value is dependent upon E_λ , defined as the difference between the switching (E_{sw}) and reversible potentials, as well as upon the rate of any chemical reactions coupled to charge transfer. Theoretical data were obtained by digital simulation⁷ for Nernstian charge transfer in the absence of coupled reactions with E_λ ranging from 100 to 500 mV. The data are summarized in Table 1. The normalization factors given in the last column are equal to R_I for Nernstian charge transfer. An experimental R_I when divided by the appropriate normalization factor will be equal to 1 for Nernstian charge transfer processes in the absence of chemical complications.

The CV data in Table 2 refer to the reduction of fluoren-9-one in DMF containing Bu_4NBF_4 . The normalized peak current ratios (R_I)_N were calculated using the appropriate factors listed in Table 1. The data indicate that this system fits the Nernstian no-reaction case

Table 1. Normalization Factors for Cyclic Voltammetry Peak Current Ratios derived From Nernstian Charge Transfer.^a

E_λ /mV ^b	I_{max}	I_{min}	Normali- zation Factor ^c
100	0.4463	-0.2556	0.5727
150	0.4463	-0.2876	0.6444
200	0.4463	-0.3077	0.6872
250	0.4463	-0.3216	0.7206
300	0.4463	-0.3320	0.7439
350	0.4463	-0.3402	0.7623
400	0.4463	-0.3468	0.7771
450	0.4463	-0.3524	0.7896
500	0.4463	-0.3571	0.8001

^a Theoretical data obtained by digital simulation. ^b The difference in the switching and reversible potentials. ^c The absolute value of the peak current ratio for Nernstian charge transfer in the absence of double layer charging current.

Table 2. Determination of Cyclic Voltammetry Peak Current Ratios during the Reduction of Fluoren-9-one in DMF.^a

$-E_{\lambda}/V$	$-E_{\text{Start}}/V$ vs. Ag/Ag^+	R_I	$(R_I)_N^b$
0.100	1.026	0.5734(0.0009)	1.0013
0.150	1.076	0.6420(0.0002)	0.9963
0.200	1.126	0.6882(0.0002)	1.0015
0.250	1.176	0.7215(0.0003)	1.0012
0.300	1.226	0.7472(0.0003)	1.0045
0.350	1.276	0.7668(0.0003)	1.0059
0.400	1.326	0.7827(0.0002)	1.0072
0.450	1.376	0.7911(0.0002)	1.0019
0.500	1.426	0.8010(0.0002)	1.0011

^a Measurements in solvent containing fluoren-9-one (1.00 mM) and Bu_4NBF_4 (0.10 M) at 295 K at a voltage sweep rate of 1.00 V/s. ^b Calculated using the normalization factors in Table 1.

Table 3. A Comparison of Electrochemical Relaxation Methods for the Measurement of the Rate Constant for A Dimerization Reaction.^a

Technique	V_c^b	$k/M^{-1} s^{-1}$
DPSC	$\tau_{\frac{1}{2}}$ (3.47 ± 0.03 ms)	1.49×10^5
DCV	$v_{\frac{1}{2}}$ (53.9 ± 0.5 V/s)	1.67×10^5
CV	$v_{0.3}$ (78.8 ± 0.7 V/s)	1.79×10^5

^a Data for the dimerization of 9-cyanoanthracene anion radical in DMF containing Bu_4NF_4 (0.1 M) and HOAc (8.8 mM) at 281.7 K. Measurements at a mercury electrode. ^b The value of the variable, pulse width or sweep rate, necessary for a predetermined value of the observable. The values are the means and standard deviations resulting from 5 determinations.

very closely under the conditions of the measurements over the entire range of E_{λ} . The standard deviations in 5 determinations of R_I were equal, on the average, to about 0.05 % of R_I which indicates a negligible error in the measurement of R_I . The deviations in $(R_I)_N$ from unity were considerably larger (0.4 % on the average) but still not serious.

The ultimate use of peak current ratios in CV is for the evaluation of rate constants of chemical reactions coupled to charge transfer. In order to demonstrate the use of R_I as defined in eqn. (1), a well defined process was chosen as a model reaction. For this process considerable experimental data are available. The process involves the reduction of 9-cyanoanthracene (AN-CN) in DMF in the presence of acetic acid. Under these conditions²⁰ the reaction can be described by eqns. (2)–(4) and rate law (5).



$$-d[(\text{AN-CN})^{\cdot -}]/dt = k_3[(\text{AN-CN})^{\cdot -}]^2 \quad (5)$$

The dimerization has previously been studied by derivative cyclic voltammetry (DCV)^{20,21} and by double potential step chronoamperometry.^{20,22} In the presence of acetic acid the kinetics are simplified²⁰ since rapid reaction (4) precludes reverse reaction (3). The data in Table 3 provide a comparison of the precision and the rate constants obtained by DPSC, DCV and CV according to eqn. (1). Rate constants were evaluated by comparing experimental data with the corresponding theoretical values obtained by digital simulation of mechanism (2)+(3).

All of the experimental data in Table 3 were obtained on the same solution of 9-cyanoanthracene (1.6 mM) in DMF containing Bu₄NBF₄ (0.1 M) and acetic acid (8.8 mM) at 281.7 K. Values of k were obtained successively using each of the techniques. The sequence was repeated until 5 k were determined using each of the three techniques. The values given in Table 3 are the means and standard deviations in the five replicates. The standard deviations were slightly less than 1 % of the mean values in all three cases. Thus, the measurement precision appears to be very nearly the same for DPSC, DCV and CV for experiments carried out on the same solution using the same apparatus.

The mean value of the rate constant obtained using all three techniques was $1.65 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ with a standard deviation of $\pm 9 \%$. It is not clear what causes the deviations in the rate constants. The deviations are clearly far out of the range of experimental error. The rate constants obtained by DCV previously²⁰ were also about 10 % larger than those obtained by DPSC under the same conditions. It is also not clear which of the three values of the rate constant determined can be considered to be most reliable. This is a problem which warrants further detail study. The conclusion can be drawn that CV using eqn. (1) gives rate constants in good agreement with those from DPSC and DCV with comparable precision.

CONCLUSIONS

It is important to keep in mind the conditions under which ordinary CV, as described in this paper, can be expected to give acceptable kinetic data. Eqn. (1) explicitly assumes that only faradaic and double layer charging current are involved in the voltammetric waves and that the double layer charging current is equal but opposite in sign on the forward and backward scans of the CV. When this is the case, ordinary CV, as demonstrated by the data in Tables 2 and 3, gives data as precise as that available from DCV or DPSC measurements. When these conditions do not prevail, eqn. (1) is not valid and CV measurements will not be capable of producing quantitative kinetic data. Thus, it is important to experimentally evaluate the validity of eqn. (1) under the conditions that measurements are to be made before collecting kinetic data.

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